Uranyl(VI) Complexes of 3-Aminopropanoic Acid and 4-Aminobutanoic Acid in Aqueous Solution: a Potentiometric and Calorimetric Study

Arturo Bismondo* and Luigi Rizzo
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., C.so Stati Uniti, 35100 Padua, Italy
Plinio Di Bernardo* and Pier Luigi Zanonato
Dipartimento di Chimica Inorganica Metallorganica ed Analitica dell'Università, Via Loredan 4, 35131 Padua, Italy

Using potentiometric and calorimetric measurements, the stability constants and the enthalpy changes of the uranyl(VI) complexes with 3-aminopropanoic and 4-aminobutanoic acids in aqueous 1 mol dm^{-3} sodium perchlorate at 25 °C have been determined. The uranyl(VI) ion has been found to form three successive entropy-stabilized mononuclear complexes with both the amino acids. The values of the stability constants indicate that the interaction of the amino acids proceeds without any involvement of the amino group. In addition, due to the ionic character of these interactions, a simple equation, based on electrostatic interaction between cation and anion, is shown to reproduce well the free energy changes relative to the formation not only of the first, but also of the second and third uranyl(VI)–amino acid complexes. A comparison between the entropy and enthalpy changes for the complexation of uranyl(VI) by amino acids and some monocarboxylate anions indicates that the amino acid complexes are generally more solvated.

In the last decade much work has been performed to determine the stoicheiometries and the stability constants of complexes between several metal ions and amino acids or peptides.[1] The main goal of these investigations was to obtain a model to establish the nature of the interactions between metal ions and proteins. A literature survey on these data reveals that binding sites, complex stabilities, and stoicheiometries are well defined for a great number of adducts between amino acids and *d*-block ions, while a remarkable disagreement was found on the complexation of the *f*-block elements. The main contradictions concern the maximum number of ligands that may be co-ordinated to the metal ion and the chelating ability of the amino acids. These are, in fact, considered chelating agents toward *f*-block elements by some authors,[2] while, according to others,[3] the amino nitrogen is not involved in complex formation. Probably, due to this contradictory information, the stability constants and, when available, the corresponding enthalpy and entropy changes of uranyl(VI)–amino acid complexes are not reported in the critical compilations.[1] The formation of amino acid chelate complexes for both lanthanides[4] and uranyl(VI)[5] ions was however excluded by some recent reports. The crystal structures of the uranyl(VI)–amino acid[6] complex $[UO_2(HL)_3][ClO_4]_2$ (HL = 4-aminobutanoic acid) and of $[Nd_2(Gly)_6][ClO_4]_6 \cdot 9H_2O$ (Gly = glycine)[7] strongly support this hypothesis.

In previous papers we dealt with the thermodynamic data concerning the formation of uranyl(VI)–monocarboxylate[8] and –glycine[5b] complexes. We now report on the results of a potentiometric and calorimetric study on the complexation of uranyl(VI) by 3-aminopropanoic acid (β-alanine) and by 4-aminobutanoic acid. This study was undertaken to clarify the role of the different structure and charge of the anions on the thermodynamic functions that preside at the formation and stability of the uranyl(VI) complexes.

Experimental

Stock solutions of $UO_2(ClO_4)_2$ containing an excess of perchloric acid and stock solutions of $NaClO_4$ were prepared and standardized as reported.[8]

The solutions of the amino acids (Baker Analyzed Reagent) were prepared by weight, after the commercial products were recrystallized from water–ethanol (1:1) mixtures and dried at 110—120 °C. They were titrated every time by potentiometry with sodium hydroxide. The 3-aminopropanoic acid solutions were titrated in the presence of formaldehyde.[2b]

The potentiometric and calorimetric measurements on the uranyl(VI) ion were carried out by adding a known amount of an amino acid solution to a known volume of a solution containing the metal ion ($c_M{}^0$ = 10—30 mmol dm^{-3}) and perchloric acid ($c_H{}^0$ = 10—15 mmol dm^{-3}). Because of the high tendency of the free uranyl ion to hydrolyze, the investigations were limited to pH < 3.5. At these values of pH the only ligand available to the uranyl(VI) ion is the zwitterion HL $[H_3{}^+N\text{–}(CH_2)_n\text{–}COO^-]$ which is known from the already studied uranyl(VI) amino acetic acid system[5b] to form rather weak complexes. Therefore, to increase the ligand concentration without increasing the pH excessively, buffer solutions were used. These were prepared by adding standard $HClO_4$ to the HL solutions until the required H_2L^+:HL ratios were reached.

The proton–amino acid systems were studied by adding standard $HClO_4$ to 10—50 mmol dm^{-3} solutions of the amino acids. In this way, only the thermodynamic parameters referring to the protonation of the carboxylic group were determined. The protonation of the amino group was not studied because, as remarked above, we do not consider that it is involved in complex formation. Other details on the potentiometric and calorimetric measurements are given in refs. 5*b* and 9.

All measurements were carried out at 25 °C and in 1 mol dm^{-3} $NaClO_4$ as constant ionic medium. Calculations were performed by a CDC computer using the programs MINIQUAD 75 and LETAGROP KALLE.[10,11]

Results and Discussion

The dissociation constants and the thermodynamic parameters for the protonation of the carboxylate group of the ligands are listed in Table 1.

For 3-aminopropanoic acid, good agreement has been found between the pK_a determined in this work and that available in the literature,[12] obtained under the same experimental conditions. On the contrary, the value we found for the carboxylate protonation of 4-aminobutanoic acid is slightly different from that reported in ref. 13 (pK_a = 4.07 in 1 mol dm^{-3} NaCl).

The stability constants for the formation of the complexes are given in Table 2, together with the corresponding overall enthalpy and entropy changes. In addition to these results, the literature data concerning the complexation of the uranyl ion by glycine[5b] and some other monocarboxylate anions[8] are reported for comparison. In Figure 1, logarithmic plots of the stability constants β_j of these complexes *vs.* the pK_a values of the carboxylic acids are reported. The log β_j values for the formation of uranyl(VI)–amino acid complexes follow the same trend observed for the formation of monocarboxylate complexes. This is good evidence for the interaction of the amino acids proceeding without any involvement of the amino group. We will now discuss the analogies and differences in the thermodynamic functions involved in the formation of the uranyl complexes with these two categories of ligands.

It is well known that the uranyl(VI) ion forms 1:1 monocarboxylate complexes the stability (log β_1) of which strongly depends on the basicity of the ligands (pK_a values). This mainly reflects the ionic character of these interactions. The investigations on the uranyl(VI) monocarboxylate complexes so far carried out[14] were confined to the observation of this evidence and to a mainly qualitative interpretation of these phenomena. Recent studies on the complexing ability of lanthanide(III) and actinide-(III) and -(IV) ions with carboxylate ligands have pointed out that the free energy changes relative to the complex formation are well reproduced by a simple equation based on the electrostatic interaction.[15] To simulate the 1:1 complex formation this equation was modified by Choppin[16] to give equation (1); units of ΔG° are kJ mol^{-1}. The quantities Z_1 and

$$\Delta G^{\circ} = -(1\,387\,Z_1Z_2)/(D_e d_{12}) - RTv \ln 55.5 + RT\Sigma \ln f(\mu) \quad (1)$$

Z_2 in the first term stand for the metal and ligand ionic charges respectively; D_e is the medium effective dielectric constant, d_{12} represents the internuclear distance (Å) of the ionic couple in the complex. The second term accounts for the cratic effect and v depends on the species number variation on the complex formation. Finally $\Sigma \ln f(\mu)$ accounts for the ionic medium in which the free energy changes have been measured (see ref. 16 for further details).

A linear relationship exists between log β_j and the pK_a for the formation of all the complexes, as shown in Figure 1; moreover the ratio of the slopes of the three lines is *ca.* 1:2:3, the actual values being 0.70, 1.33, and 1.92 respectively. As a consequence, the Choppin equation can be reasonably applied not only to the first of these successive reactions but also to the second and the third; in fact for the latter two reactions, the Z_2 value, which represents the charge of the negative ions surrounding the cation, increases in the same ratio of 1:2:3 on going from the first to the second and to the third complex.

On the basis of the above observations, we applied equation (1) to the formation of all the consecutive uranyl(VI) complexes. The variables in the equation were set as follows. The actual uranyl(VI) charge[16] was set to +3.3, and the internuclear distance d_{12} to 2.4 Å,[4] mean distance U–O(carboxylic) found[17] in some uranyl(VI)–monocarboxylate complexes in the solid state, while the value of Z_2 was estimated according to the following considerations. The increase of the pK_a of a carboxylic group can be attributed to an increase of its charge density. A charge of −1 can be reasonably attributed to the carboxylic group of an acid with a pK_a value of 5, which is the upper limiting value for aliphatic monocarboxylic acids.[18] The effective charge for each of the considered anions, Z_2, can be successively calculated by setting constant all the values in equation (1), except the free energy of the ligand protonations. In this way, we established that $Z_2 = 0.243 + 0.151$ pK_a. By substituting the preceding values and the corresponding formation energies of the complexes in equation (1), we found

Table 1. Thermodynamic parameters for the proton–carboxylate interaction: I = 1 mol dm^{-3} (NaClO$_4$), 25 °C

Amino acid	pK_a	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
3-Aminopropanoic acid	3.77 ± 0.02	−5.7 ± 0.2	53 ± 1
4-Aminobutanoic acid	4.25 ± 0.03	−3.8 ± 0.2	69 ± 2

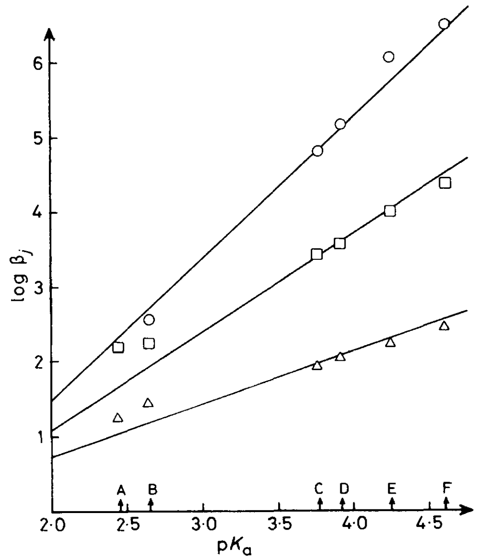

Figure 1. Logarithm of the formation constants of some uranyl(VI)–monocarboxylate and -amino acid complexes as a function of pK_a: (△) log β_1, (□) log β_2, (○) log β_3. The solid lines represent log β_j values calculated by equation (1). A = Aminoacetic acid, B = chloroacetate, C = 3-aminopropanoic acid, D = 3-chloropropanoate, E = 4-aminobutanoic acid, F = acetate

Table 2. Comparison of thermodynamic values[a] for the complexation of uranyl(VI) with some amino acids and monocarboxylates: I = 1 mol dm^{-3} (NaClO$_4$), 25 °C

Ligand	pK_a	log β_1	log β_2	log β_3	ΔH_1°	ΔH_2°	ΔH_3°	ΔS_1°	ΔS_2°	ΔS_3°	Ref.
Aminoacetic acid	2.46	1.16	2.20		3.9	4.8		35	58		5*b*
Chloroacetate	2.66	1.44	2.24	2.57	8.0	16.1	24.4	54	97	131	8
3-Aminopropanoic acid	3.77(2)	1.93(2)	3.44(3)	4.82(5)	6.5(2)	12.0(3)	11.3(4)	59(1)	106(2)	130(3)	*b*
3-Chloropropanoate	3.92	2.06	3.58	5.18	11.3	20.9	20.9	77	139	169	8
4-Aminobutanoic acid	4.25(3)	2.25(1)	4.02(2)	6.08(3)	10.6(3)	15.5(4)	13.0(6)	79(1)	129(2)	160(3)	*b*
Acetate	4.61	2.46	4.38	6.52	11.8	17.9	16.8	87	144	181	8

[a] ΔH° in kJ mol^{-1}, ΔS° in J K^{-1} mol^{-1}; estimated standard deviations are given in parentheses. [b] This work.

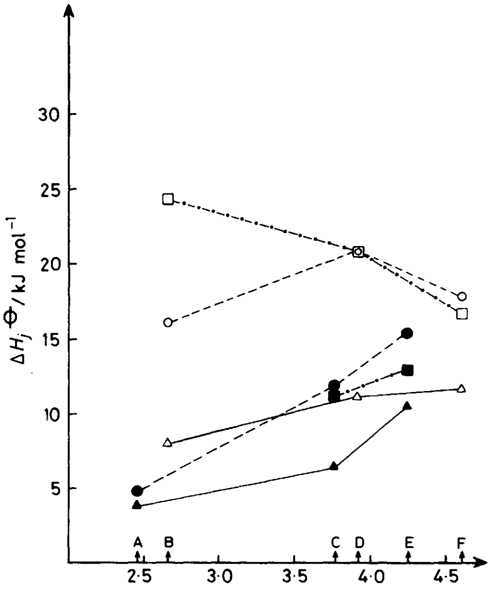

Figure 2. Correlation between $\Delta H_j^{\ominus}$, the total enthalpy of complexation, and ligand pK_a values for the formation of some uranyl(VI) complexes with monocarboxylates (open symbols) and amino acids (full symbols): (△,▲) $\Delta H_1^{\ominus}$, (○,●) $\Delta H_2^{\ominus}$, (□,■) $\Delta H_3^{\ominus}$. For A—F, see Figure 1

that the D_e values, giving the best approximation of the experimental data, were 72, 76, and 79 for the formation of the first, second, and third uranyl(VI) complexes respectively. The above values were used in equation (1) to obtain, with some rearrangement, equation (2) that relates log β_j to pK_a and is represented by solid lines in Figure 1.

$$\log \beta_j = (81.2 + 50.4\ \mathrm{p}K_a)/D_e + 1.744\ \nu - \Sigma \log f(\mu) \quad (2)$$

The variables ν and $\Sigma \log f(\mu)$ in equation (*2*) were given the following values: $\nu = -1, -2, -3$; $\Sigma \log f(\mu) = 0.109, 0.531$, and 0.531 for $j = 1, 2$, and 3 respectively. The good agreement between the experimental data and the calculated values indicates the following. (*a*) A relation based on the electrostatic interaction between anion and cation can be used for the formation not only of the first complex, but also for the successive ones. (*b*) The complex stabilities appear to be independent of the structure, dimensions, and formal charge of the ligands (amino acids have zero formal charge) and related only to the actual charge present on the carboxylic group.

As shown in Figure 1, the experimental values of log β_j for the less basic ligands (aminoacetic acid and chloroacetate) are slightly higher than that expected on the basis of the linear relationship. This may indicate the presence in solution of outer-sphere complexes. In fact, Choppin[16] found that for the formation of the complexes between lanthanum and chloroacetates ($Cl_nCH_{3-n}COO^-$, n = 0—3), the fraction of inner-sphere complexes in solution as determined by means of $^{139}La^{III}$ n.m.r. spectroscopy agrees with that calculated by using a value of β_i (i = inner) obtained by equation (2). For the complexation of Am^{III} by the same ligands, he found that the experimental stability constants (β_{ex}) of complexes with ligands having low pK_a were higher than if calculated by equation (2). These results were rationalized by assuming the formation in solution of outer-sphere complexes the stability constant of which (β_o, o = outer) was obtained by $\beta_o = \beta_{ex} - \beta_i$. These studies also proved that the relative amount of inner-sphere complex in solution increases with the ligand pK_a; so there is a critical value of pK_a under which outer-sphere complexation is dominant while above it inner-sphere complexes are expected. The change from mostly inner- to mostly outer-sphere complexation is reported[16] to be at pK_a *ca.* 1.7 for the actinyl MO_2^{2+} ions. Such evidence suggests that, in the present case, a certain amount of outer-sphere complexes, for which equation (2) is not valid, is probably formed.

The relationship between the measured enthalpy changes and the basicity of the ligands is shown in Figure 2. The $\Delta H_j^{\ominus}$ values for the formation of the uranyl(VI) complexes with monocarboxylate ions are clearly higher than those for the complexes with amino acids of comparable basicity. So, it is interesting to consider the enthalpy changes for complexation of the uranyl(VI) ion by two sets of ligands similar in basicity but different in structure: 4-aminobutanoic acid *versus* acetate and, 3-aminopropanoic acid *versus* 3-chloropropanoate. The difference between the $\Delta H_j^{\ominus}$ values increases with the number of ligands co-ordinated to the central atom, and with the decrease of the ligand basicities. The differences in $\Delta H_1^{\ominus}$, $\Delta H_2^{\ominus}$, and $\Delta H_3^{\ominus}$ are, in fact, 1.2, 2.4, and 3.8 kJ mol^{-1} respectively for the first set (more basic ligands) and 4.8, 8.9, and 9.6 kJ mol^{-1} for the second one. In Figure 2 two different trends in $\Delta H_j^{\ominus}$ values are evident. In the formation of the complexes with chloroacetate, 3-chloropropanoate, and acetate, $\Delta H_1^{\ominus}$ increases, $\Delta H_2^{\ominus}$ is indeterminate, and $\Delta H_3^{\ominus}$ decreases with pK_a. For the formation of amino acid complexes, however, $\Delta H_j^{\ominus}$ increases always with pK_a. The entropic variation (see Table 2) for the formation of uranyl(VI) complexes with amino acids is in any case lower than for that of similar adducts with carboxylate ligands of comparable basicity.

This trend of the thermodynamic functions can be explained by the ionic model which assumes that the formation of complexes depends on the variation of the solvation sphere mainly of the cation and, only to a lower extent, of the ligand. The uranyl(VI) ion, with its high charge:radius ratio, is strongly solvated in aqueous solution. When an inner-sphere complex is formed the hydrated structure around the metallic cation collapses because the negative charge on the ligands partially neutralizes the charge of the metallic cation and the ligand hydrophobic alkyl chains introduce a further element of disorder in the solvation sphere of the complex. The breaking of the ion–water and water–water bonds in the hydrated species requires a remarkable amount of energy, which is only partially balanced by the formation of a new bond in the complex. So, the formation enthalpy of the complexes is endothermic. On the other hand, the complexation decreases the ion solvation and consequently the randomness of the system and the entropy content increase. This causes the reaction to occur in spite of the unfavourable enthalpy term.

According to these considerations, the data available on the enthalpy and entropy changes for the uranyl(VI) complex formation can be rationalized as follows. The increase of $\Delta H_1^{\ominus}$ and $\Delta S_1^{\ominus}$ with pK_a indicates a progressive decrease in the solvation of the complex, probably because of the higher charge neutralization caused by the more basic ligands. In other words, the more effective is the interaction, the higher is the desolvation energy counteracting the formation of the first complex. Nevertheless, the increase of the absolute value of $\Delta G_1^{\ominus}$ with pK_a shows that the energy produced by the interaction of the uranyl(VI) ion with more basic ligands greatly surpasses the heat quantity required by the breaking of the hydration shell of the reacting ions.

On going from the 1 : 1 to the 1 : 3 complex formation, the total amount of energy required, mainly by the desolvation of the cation and to a lesser extent by the dehydration of the ligands, increases. On the other hand, the energy produced by the electrostatic metal–ligand interaction increases with pK_a so that the compensation of these two opposite terms [ΔH(dehydration) > 0, ΔH(interaction) < 0] explains satisfactorily the trends shown in Figure 2.

The lower values of ΔH_j° and ΔS_j° for the interactions of amino acids with the uranyl(VI) ion can be explained by the presence of the charged group in the ligand chain which produced an ordering effect towards the solvent around the complex. This observation is supported by the large value of the hydration enthalpy ($\Delta H^{\circ} = -365.4$ kJ mol^{-1}) of the protonated glycine ($HGly^+$) recently reported.[19] Thus we suggest that the uranyl(VI)–amino acid complexes on the whole are more solvated than those formed by other ligands of comparable basicity. As a consequence of the lower desolvation energy, the enthalpy change becomes more favourable (less endothermic) and the reaction entropy less favourable (less positive) to the complex formation. Due to these counteracting variations, the stability constants are little influenced by the protonated ammonio group in the chain.

Acknowledgements

The experimental data acquisition and monitoring system was designed and implemented with a substantial contribution from Dr. G. Trainito, Istituto di Dinamica dei Sistemi e di Bioingegneria del C.N.R. (Padova), to whom we wish to express our deep gratitude.

References

1 A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum Press, New York, 1974, vol. 1 and 1st Supplement, 1982, vol. 5.

2 (*a*) M. Cefola, R. C. Taylor, P. S. Gentile, and A. V. Celiano, *J. Phys. Chem.*, 1962, **66**, 790; (*b*) M. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290; (*c*) O. Farooq, A. U. Malik, N. Ahmad, and S. M. F. Rahman, *J. Electroanal. Chem. Interfacial Electrochem.*, 1970, **24**, 464; (*d*) G. M. Sergeev and I. A. Korshunov, *Sov. Radiochem. (Engl. Transl.)*, 1973, **15**, 623; (*e*) A. Raghavan and M. Santappa, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3363; (*f*) K. Rengaraj and V. V. Ramanujam, *Indian J. Chem., Sect. A*, 1976, **14**, 451.

3 N. C. Li, E. Doody, and J. M. White, *J. Am. Chem. Soc.*, 1958, **80**, 5901; I. Feldman and L. Koval, *Inorg. Chem.*, 1963, **2**, 145; S. P. Tanner and G. R. Choppin, *ibid.*, 1968, **7**, 2046; V. V. Ramanujam, K. Rengaraj, and B. Sivasankar, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2713.

4 R. Prados, L. G. Stadtherr, H. Donato, jun., and R. B. Martin, *J. Inorg. Nucl. Chem.*, 1974, **36**, 689 and refs. therein.

5 (*a*) V. V. Ramanujam and K. Rengaraj, *Indian J. Chem., Sect. A*, 1980, **19**, 382; (*b*) A. Bismondo, L. Rizzo, G. Tomat, D. Curto, P. Di Bernardo, and A. Cassol, *Inorg. Chim. Acta*, 1983, **74**, 21; (*c*) N. W. Alcock, D. J. Flanders, T. J. Kemp, and M. A. Shand, *J. Chem. Soc., Dalton Trans.*, 1985, 517.

6 A. Bismondo, U. Casellato, E. Forsellini, and R. Graziani, *J. Cryst. Spectrosc. Res.*, 1985, **15**, 257.

7 J. Legendziewicz, E. Huskowska, A. Waskowska, and G. Argay, *Inorg. Chim. Acta*, 1984, **92**, 151.

8 R. Portanova, P. Di Bernardo, A. Cassol, E. Tondello, and L. Magon, *Inorg. Chim. Acta*, 1974, **8**, 233.

9 P. Di Bernardo, A. Cassol, G. Tomat, A. Bismondo, and L. Magon, *J. Chem. Soc., Dalton Trans.*, 1983, 733.

10 P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

11 R. Arnek, *Ark. Kemi*, 1970, **32**, 81.

12 E. Bottari and P. Siliberti, *Ann. Chim. (Rome)*, 1976, **66**, 629.

13 E. Bottari, *Ann. Chim. (Rome)*, 1976, **66**, 193.

14 C. Miyake and H. W. Nurnberg, *J. Inorg. Nucl. Chem.*, 1969, **29**, 2411; L. Magon, R. Portanova, B. Zarli, and A. Bismondo, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1971.

15 R. Munze, *J. Inorg. Nucl. Chem.*, 1972, **34**, 661.

16 G. R. Choppin, *Radiochim. Acta*, 1983, **32**, 43.

17 J. Howatson, D. M. Grev, and B. Morosin, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1933; B. F. Mentzen, *Acta Crystallogr., Sect. B*, 1977, **33**, 2546.

18 H. C. Brown, D. H. McDaniel, and O. Hafliger, 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955.

19 M. J. Loke and R. T. McIver, jun., *J. Am. Chem. Soc.*, 1983, **105**, 4226.

Received 21*st February* 1986; *Paper* 6/393